
STUDY OF ACTIVITY AND SELECTIVITY OF OXIDE CATALYSTS IN HYDROCARBON OXIDATION REACTIONS

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ABSTRACT

The selectivity of complex reactions is one of the main problems of heterogeneous catalysis. Thus, it is known that the oxidation of hydrocarbons can proceed with the formation of soft and deep oxidation products. Finding the factors that determine one or the other direction of the reaction means obtaining a method for controlling the selectivity of the process. For a few catalytic oxidation reactions, there is reliable information about their mechanism.

Key Words: deep oxidation; C₃-C₄-olefins; the selectivity; catalytic reactions; re-oxidation.

1. INTRODUCTION

The selectivity of complex reactions is one of the main problems of heterogeneous catalysis. In catalytic transformations of organic substances, the problem of selectivity regulation faces additional difficulties due to the ability of these substances to have a different type of chemical interaction with the same catalyst, which determines the possibility of the reaction proceeding simultaneously in different directions. Thus, it is known that the oxidation of hydrocarbons can proceed with the formation of soft and deep oxidation products. To find the factors that determine this or that direction of the reaction is to obtain a method for controlling the selectivity of the process. This can be done only based on sufficiently well-founded ideas about the nature of desirable and undesirable reaction directions. For a few catalytic oxidation reactions, reliable information about their mechanism is available.

2. METHODOLOGICAL PART

It has been convincingly proven [1] that the selective oxidation of hydrocarbons on oxide catalysts proceeds according to the redox mechanism, the so-called staged or split oxidation, with the participation of oxide-oxygen. The complete oxidation of organic substances can proceed, depending on the temperature, both by the redox and the associative mechanism, in the latter case, with the participation of oxygen adsorbed on the oxide surface. The oxidation reaction by the redox mechanism consists of the alternate restoration of the oxide catalyst surface by the oxidizing substance and its re-oxidation by molecular oxygen.

The nature of the interaction of the reactants with the catalyst surface and the type of intermediates formed in this process should primarily determine the direction of the oxidation reaction. Therefore, revealing functional relationships between the kinetic regularities of catalytic reactions and the properties of catalysts is one of the most effective approaches to regulating the activity and selectivity of catalysts. The influence of the chemical composition of binary oxide catalysts (Bi-Mo, Fe-Mo, Co-Mo, Fe-Sb, Co-Sb, Sn-Sb, including their constituent oxides) and related lattice oxygen mobility E_0 , electron release work $\Delta\gamma$, electric conductivity σ , and other contact properties on their activity and selectivity concerning the indicated type of reactions was studied by the example of severe and partial oxidation reactions of C₃-C₄-olefins.

In the series of these oxides, a directly proportional relationship between E (activation energy) and E_0 (almost equality of these parameters) is realized, which indicates the participation of surface oxygen of the oxide lattice in the act of deep oxidation catalysis. The limiting stage of the observed process rate is breaking the bond between the surface oxygen and the catalyst during the chemisorption of the olefin. On this basis, it is assumed that the intermediate chemical interaction of the olefin with the oxide catalyst proceeds with the participation of surface oxygen ions and leads to the rupture of the Me-O bond. This type of interaction should be favored by a high degree of ionicity of the Me-O bond in the catalyst, low values of the E_0 parameter, and some optimal values of the catalyst electron affinity ($\Delta\gamma$).

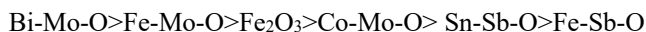
The oxides V₂O₅, MoO₃, and Sb₂O₅ are characterized by the highest values of E_0 , the lowest catalytic activity, and the absence of dependence between E and E_0 . The most probable reason for their standard action in the profound oxidation reaction is the high surface oxygen binding energy resulting from the high values of E_0 . At the same time, these oxides are characterized by the highest selectivity of catalytic activity concerning the partial oxidation reactions of olefins (by C-H bond). To achieve a selective catalytic effect, an oxide catalyst must have

a particular ability to break the C-H bond and protect the double bond of the olefin from oxidation. These requirements are met by motivations whose cations have a high acceptor capacity, which provides the ability to coordinate the binding of the olefin. The strong acceptor-donor interaction of the catalyst with the olefin increases the polarization of the C-H bond and hence the probability of exchange of surface oxygen with this bond. The ability to coordinate the binding of olefins can be indirectly judged by the value of the $\Delta\gamma$ parameter and the reduced ability of the oxide. The higher $\Delta\gamma$ and the easier the reduction ability of the oxide, the greater its ability to coordinate olefin binding. Selective catalysts must also be characterized by high oxygen binding energy (high value of E_0). This prevents the interaction of oxygen ions on the double bond. Thus, a change in the chemical composition of the catalyst that leads to a decrease in E_0 , while $\Delta\gamma$ remains unchanged or increases, should increase its activity concerning deep oxidation. If a change in the composition leads to a rise in E_0 , then the ability to selectively catalyze partial oxidation should increase. In this case, the higher $\Delta\gamma$ is, the greater the catalyst activity. The high activity and selectivity of binary oxide systems, as compared to their constituent oxides, in the partial oxidation reactions of olefins and explained by the large values of E_0 and $\Delta\gamma$ for complex systems. The higher values of E_0 for all compositions of the tin-stibium catalyst determine its more excellent selectivity for partial oxidation compared to other oxide systems. Another property of the catalyst is contact acidity [2]. It was found that catalyst acceptability and hence the strength of its bond with adsorbed olefin, which determines the direction of oxidative transformation, significantly depend on the acid-base properties of the catalyst surface. An increase in acidity leads to hardening allyl radical binding to the surface and increases the probability of oxidation of propylene to acrolein.

We found that the course of hydrocarbon oxidation reactions along different directions and catalyst selectivity is determined by the interaction between the reaction components. Experimental experiments have shown that the diverse nature of the mutual influence of hydrocarbons and oxygen during their chemisorption on the contact surface can cause soft or deep oxidation. Soft oxidation catalysts (Sn-Sb-O, copper oxide, Sn-Mo-O, MoO_3) show an increase in hydrocarbon adsorption and hence an increase in surface charge ability in the case of hydrocarbon adsorption on a partially oxygen-coated surface. On the contrary, on deep oxidation catalysts, the charge increase is observed in the case of oxygen adsorption on the surface coated with irreversibly chemisorbed olefin. The mutual enhancement of hydrocarbon and oxygen adsorption is due to the interaction of these gases under precatalyst conditions with the formation of oxygen-hydrocarbon complexes, which are intermediate forms in oxidation reactions. The first stage of the soft oxidation reaction should be the chemisorption of O_2 , and the centers of formation of the intermediate oxygen-hydrocarbon complex are the chemisorbed oxygen particles. For deep oxidation, the first step of the reaction should be the chemisorption of hydrocarbon, and the reaction centers should be chemisorbed hydrocarbon. Intermediate carbon-oxygen complexes on selective oxidation catalysts contain an excess of C atoms compared to oxygen atoms and are positively charged. On deep oxidation catalysts, the complexes have a quantity of O_2 and are negatively charged. So, the hydrocarbon-oxygen complexes active in catalysis during soft and deep oxidation of hydrocarbons are formed at different centers of the catalyst surface, have different compositions, and are oppositely charged. Various forms of oxygen adsorbed on oxide catalysts, characterized by a particular bond strength with the surface, were found by adsorption and calorimetric measurements. Since oxidation reactions (soft and partially deep) in a staged mechanism involves, as one of the stages, the breaking of oxygen bonds with the catalyst surface, the catalytic activity of oxide systems in oxidation reactions significantly depends on the strength of these bonds. The catalyst's ability to carry out the complete oxidation process by the associative mechanism implies the presence of weakly bound oxygen on its surface. Indeed, in uncomplicated cases of complete oxidation of simple molecules (H_2 , CO, CH_4), the catalytic activity of oxide catalysts exponentially increases with decreasing surface oxygen binding energy.

It has been shown in [3-4] that on all oxides leading non-selective oxidation (oxides of Co, Ca, Fe, Cr, Bi, La, Ti, Zr), a weakly bonded form of oxygen adsorption is observed, which allows us to consider it to be responsible for the implementation of oxidation by the associative mechanism. However, the oxygen bond strength is not the only factor determining the catalyst performance. The absence of weakly bonded oxygen on the catalyst surface and the presence of reactive oxygen with high bonding energy are necessary but insufficient conditions for achieving high selectivity. When these conditions are met, the specific activation of the reacting molecule plays a decisive role. Thus, at equal oxygen binding energy of bismuth molybdate and iron molybdate, their selectivity in the oxidation of butene-1 is approximately 80% [3]. This is explained by the different nature of the interaction of the oxidized substance with the surface of these catalysts. The formation of partial oxidation products involves surface oxygen of the catalyst lattice with significant bond energy, i.e., the stage mechanism of catalysis is realized. The deep oxidation of the activated form of the olefin is caused by catalyst oxygen with low bonding energy and electrophilic oxygen forms. The irreversibly adsorbed form of the olefin leads to the formation of only deep and partially destructive oxidation products; its contribution to the total amount of these products formed in the reaction depends on the nature of the catalyst and the conditions of the reaction. The amount of sorbed hydrocarbon, the nature of adsorption, and the ratio of adsorbed forms essentially depend on the state of the surface (the degree of its reduction). It was shown in [4] that olefins (propylene, isobutylene) are sorbed on the reduced catalyst (iron-molybdenum-sorbent) in smaller amounts than on oxidized catalyst; at that, on reduced

contact- in reversible and irreversible forms (by 40-50% reversibly), on oxidized contact- practically irreversibly. It is natural to expect that the selectivity of the catalyst should also be determined mainly by the degree of reduction of its surface. The selectivity of catalysts should depend not only on the bonding energy of surface oxygen but also on the mobility of the lattice bulk oxygen. The mobility of bulk oxygen, and hence the degree of its participation in the formation of the surface, is determined by the catalyst's chemical composition and crystal structure. This explains the difference in the degree of reduction of the stationary working surface and the number of oxide catalysts. It is known that for some catalysts, mainly molybdenum-containing ones, the surface state and, at the same time, the catalytic properties, in the initial period of work and under steady-state conditions, differ little. This is explained by the difference between the fully oxidized in-pairs surface and the fully oxidized surface. A correlation between the degree of reduction of the catalyst surface in the steady state and the mobility of volumetric oxygen has been established. Molybdates rank first in the series of catalysts with decreasing mobility of volumetric oxygen.



Iron-antimony and tin-antimony catalysts with low oxygen mobility operate in a partially reduced state, the degree of reduction being 50-60% and 25-5%, respectively. For such catalysts in the course of the establishment of the steady state, in parallel with the growth of the reduced contact, their activity in the oxidation of olefin decreases, and their selectivity in partial oxidation increases. The reduction in the catalytic activity of metal oxides in the propylene oxidation reaction in works [4-5] is attributed to the strong chemisorption of olefin on the catalyst surface.

In the authors' opinion [5], such a change in the catalytic properties is caused by the depletion of the surface by weakly bound oxygen, which leads to a decrease in the rate of deep oxidation and, consequently, the overall activity of the catalyst. At the same time, surface oxygen with higher bonding energy enters into intermediate chemical interaction with the olefin, which increases the selectivity of C-H bond oxidation. The absence of weakly bound oxygen even on the oxidized surface of the bismuth molybdenum catalyst explains the high selectivity of bismuth molybdate already in the initial period of operation. Thus, numerous studies have shown that the activity and selectivity of oxide catalysts depend on the state in which the contact is in the catalysis process. This is the state established due to the interaction between the catalyst and the reaction mixture. In the area of the associative mechanism, the reaction rate is determined by the decomposition of intermediate surface structures under the action of molecular oxygen. In the area of the staged mechanism, the reaction rate is limited by the interaction of the hydrocarbon with the catalyst surface. The ratio of concentrations of both types of surface compounds formed during the exchange of the hydrocarbon with the contact surface is determined by the properties of the catalyst. The proportion of carbonate-carboxylate structures is higher with the weakly bound oxygen on the contact surface. The formation of surface compounds responsible for selective oxidation is largely determined by the ability of the catalyst to interact specifically with a given hydrocarbon. By the above, high selectivity can be achieved only on catalysts with sufficiently high oxygen bond strength and some optimal hydrocarbon binding energy. Studying materials on the mechanism of hydrocarbon oxidation reactions on complex oxide catalysts, we can say that several general regularities characterizing the course of such processes have been established. However, many details of the mechanism of these reactions remain unclear. These include the mechanism of adsorption interaction of the reacting substances with the catalyst, the influence of the reactants on the contact surface state, the reasons for the observed differences in the oxidation of close homologs on the same catalyst, and others.

3. CONCLUSION

We started studying these issues with the example of the oxidation reaction of isobutylene on a tin-stibium oxide catalyst. This work aims to explore the interaction of isobutylene, oxygen, and mixtures with the surface of Sn-Sb-O- catalyst, to find out the causes of changes in the catalytic contact properties under the influence of the reaction mixture, to study the relative adsorption and reactivity of C₃-C₄ olefins.

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